

(12) PATENT APPLICATION
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. AU 199894057 A1

(54) Title

(51)⁷ International Patent Classification(s)
C22B 005/14 C22B 034/12

(21) Application No: **199894057**

(22) Application Date: **1998.11.23**

(43)

(43) Publication Journal Date : **2000.05.25**

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Abstract

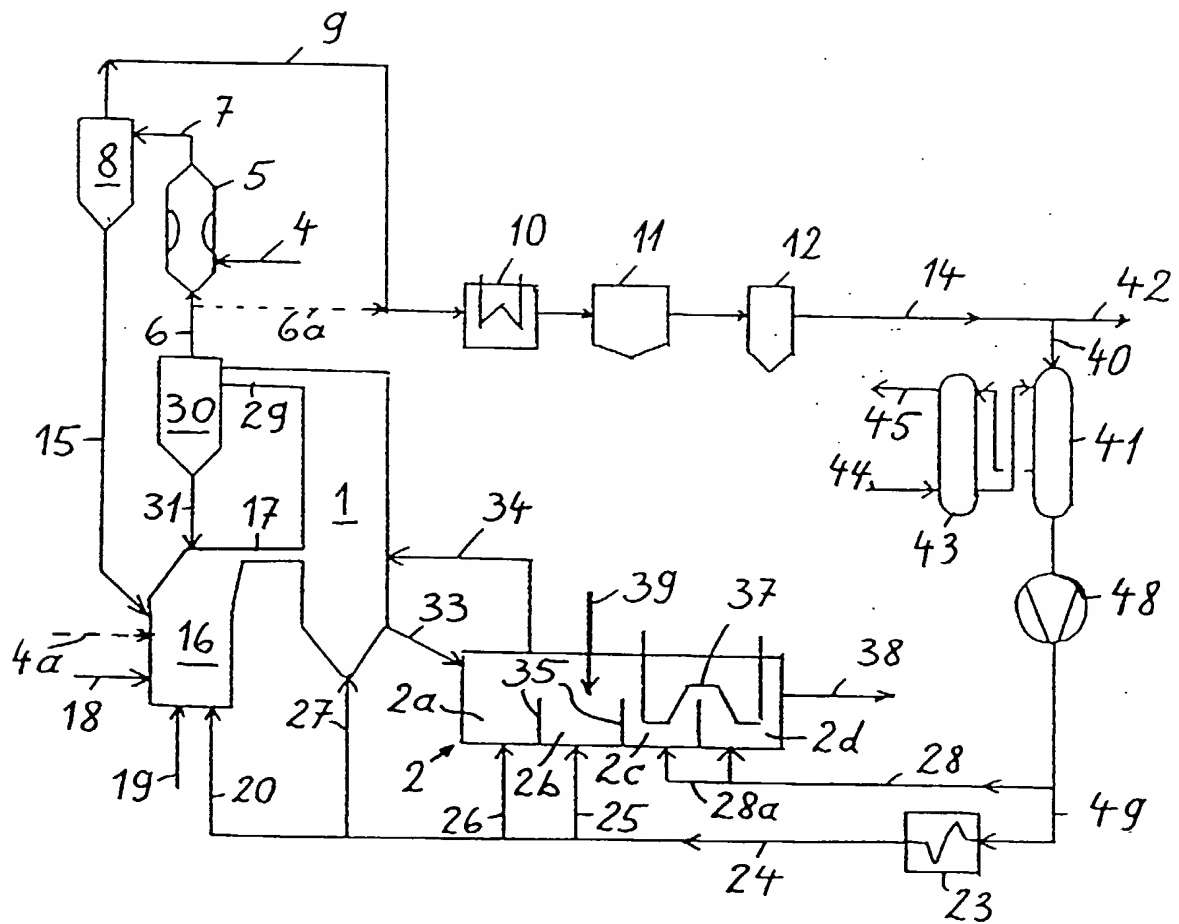
The ilmenite to be reduced has a titanium dioxide content of 45 to 65 wt-% and a content of iron oxides of 30 to 50 wt-%. In a first fluidized-bed reactor the ilmenite is partly reduced to a degree of metallization of 50 to 90 %, based on the iron oxides, and in a second reactor, which contains at least one stationary fluidized bed, the ilmenite is reduced to a metallization of 85 to 98 %, based on the iron oxides. Reducing fluidizing gas with temperatures in the range from 600 to 1000°C and a (H₂ + CO) content of 80 to 100 vol-% is supplied to both reactors. From the upper portion of the first fluidized-bed reactor solids are supplied to a separator together with a gas stream, and in said separator solids are at least partly separated from the gas stream, and separated solids are at least partly recirculated to the first fluidized-bed reactor. The amount of solids recirculated every hour to the first fluidized-bed reactor is 5 to 25 times the amount of solids contained on average in the first fluidized-bed reactor. Exhaust gas from the second reactor is introduced into the first reactor.

~~Claims~~

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process of reducing ilmenite, which has a titanium dioxide content of 45 to 65 wt-% and a content of iron oxides of 30 to 50 wt-%, characterized in that in a first fluidized-bed reactor the ilmenite is partly reduced to a degree of metallization of 50 to 90 %, based on the iron oxides, and in a second reactor, which contains at least one stationary fluidized bed, the ilmenite is reduced to a metallization of 85 to 98 %, based on the iron oxides, where reducing fluidizing gas with temperatures in the range from 600 to 1000°C and a (H₂ + CO) content of 80 to 100 vol-% is supplied to both reactors, that from the upper portion of the first fluidized-bed reactor solids are supplied to a separator together with a gas stream, and in said separator solids are at least partly separated from the gas stream, and separated solids are at least partly recirculated to the first fluidized-bed reactor, where the amount of solids recirculated every hour to the first fluidized-bed reactor is 5 to 25 times the amount of solids contained on average in the first fluidized-bed reactor, and that exhaust gas from the second reactor is introduced into the first reactor.
2. The process as claimed in claim 1, characterized in that the gas stream withdrawn from the separator of the first reactor is cooled, dedusted and partly liberated from steam, and at least part of the gas stream with a CO₂ content of not more than 5 vol-% is recirculated as fluidizing gas.
3. The process as claimed in claim 1 or 2, characterized in that in an oxidation stage the ilmenite is heated to temperatures in the range from 600 to 1000°C by combustion with air in a circulating fluidized bed, before it is charged into the first reactor, and that from the flu-

Fig. 1



AUSTRALIA

Patents Act 1990

**ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT**

Application Number:

Lodged:

Invention Title:

PROCESS OF REDUCING ILMENITE

The following statement is a full description of this invention, including the best method of performing it known to us :-

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Case No. 98 01 03

Process of Reducing Ilmenite

Description

This invention relates to a process of reducing ilmenite which has a titanium dioxide content of 45 to 65 wt-% and a content of iron oxides of 30 to 50 wt-%. The reduced ilmenite can then be further processed to obtain for instance synthetic rutile with a TiO_2 content of more than 90 wt-%.

The reduction of ilmenite and also the further processing to obtain synthetic rutile are known from GB 23 15 742 A. For reduction purposes, a plurality of stationary fluidized beds are employed. In the US-Patent 5,403,379 it is described to perform the reduction of the ilmenite in a rotary tube.

It is the object underlying the invention to perform the reduction of the ilmenite in a manner suitable for commercial plants and to operate as inexpensively as possible. In accordance with the invention this is achieved in that in a first fluidized-bed reactor the ilmenite is partly reduced to a degree of metallization of 50 to 90 %, based on the iron oxides, and in a second reactor, which contains at least one stationary fluidized bed, the ilmenite is reduced to a metal-

lization of 85 to 98 %, based on the iron oxides, where reducing fluidizing gas with temperatures in the range from 600 to 1000°C and a ($H_2 + CO$) content of 80 to 100 vol-% is supplied to both reactors, that from the upper portion of the first fluidized-bed reactor solids are supplied to a separator with a gas stream, in which separator solids are at least partly separated from the gas stream, and separated solids are at least partly recirculated to the first fluidized-bed reactor, where the amount of solids recirculated every hour to the first fluidized-bed reactor is about five to twentyfive times the amount of solids contained on average in the first fluidized-bed reactor, and that exhaust gas from the second reactor is introduced into the first reactor. The pressure in the two reactors usually is 1 to 10 bar.

The circulation of solids connected with the first fluidized-bed reactor via the reactor to the separator and back to the reactor provides for high reaction rates and at the same time long dwell times of the solids in the reactor. The coupling with the second reactor leads to a high degree of metallization while at the same time optimally utilizing the fluidizing gas. Expediently, the exhaust gas withdrawn from the first fluidized-bed reactor is at least partly reused as fluidizing gas after processing the same (e.g. dedusting and, if necessary, removal of CO_2).

When the crude ilmenite has a relatively high content of FeO , an oxidative pretreatment prior to the reduction may become necessary, as the FeO is present with a crystal lattice structure which largely resists the attack of the reducing gas. Only the conversion of FeO to Fe_2O_3 with the related conversion of the crystal lattice facilitates the subsequent reduction. Expediently, the ilmenite is heated in an oxidation stage by combustion with air in a circulating fluidized bed to temperatures in the range from 600 to 1000°C, before it is charged into the first reactor. From the fluidized bed

of the oxidation stage an exhaust gas with an O_2 content of 3 to 10 vol-% and mostly 4 to 8 vol-% is withdrawn. The O_2 content of the exhaust gas reveals that the fluidized bed of the oxidation stage provides favorable conditions for the oxidation of FeO to obtain Fe_2O_3 . Usually it is ensured that the ilmenite withdrawn from the oxidation stage contains not more than 5 wt-% and preferably not more than 3 wt-% FeO .

An advantageous embodiment of the second reactor consists in that it has 2 to 6 chambers disposed one beside the other, where each chamber contains a stationary fluidized bed. The solids are moving one after the other through all chambers in which iron oxides are reduced. In this way, high solid dwell times and a good utilization of the reducing gas are also achieved in the second reactor.

One embodiment of the process consists in that coal and carbon monoxide obtained therefrom are employed as reducing agents, and fluidizing gases chiefly consisting of CO are supplied to the first and the second reactor. In a gasifier, granular coal is partially oxidized with O_2 -containing gas, and a mixture containing hot gases and char with temperatures of 900 to 1200°C is introduced from the gasifier into the first reactor. In the first reactor there is thus obtained a temperature of preferably at least 900°C. Exhaust gas containing CO is withdrawn from the first reactor, dedusted and largely liberated from CO_2 , before it is recirculated to the two reactors as fluidizing gas.

Embodiments of the process will be explained with reference to the drawing, wherein:

Fig. 1 represents a flow diagram of the process using coal as a source for the reducing agent, and

Fig. 2 represents a further flow diagram of the process, where hydrogen is used as main reducing agent.

In accordance with Fig. 1, the reduction of the ilmenite is effected in the first fluidized-bed reactor 1 and then in the second fluidized-bed reactor 2. The crude, granular ilmenite is supplied via line 4 and for preheating purposes charged into a Venturi heat exchanger 5, to which hot exhaust gases are supplied through line 6. In direct contact with the hot gases, the ilmenite is carried to the top and supplied through line 7 to a cyclone 8. At this point, gases and solids are separated, where the hot exhaust gas is supplied through line 9 first of all to a waste heat boiler 10 and then through a dry dedusting 11 and a wet dedusting 12. Via lines 14 and 40, cooled and dedusted exhaust gas flows to a washing column 41 for removing CO_2 . Part of the gas is removed from the process through line 42. Washing to largely remove the CO_2 is effected in a known manner with a washing solution, which upon usage is reprocessed in the regenerator 43 and then recirculated. Heating steam is supplied to the regenerator 43 through line 44, CO_2 escapes via line 45. The gas, which chiefly consists of CO and H_2 , is supplied by means of the blower 48 as a cold gas in a partial stream through line 28 to the cooling portion of the reactor 2. The remaining gas flows in the branch line 49 to the fired heater 23 and from there is further utilized as hot fluidizing gas.

Preheated ilmenite comes from the cyclone 8 and through line 15 is first of all delivered to a gasifier 16, and through a passage 17 carrying hot solids and gases it is introduced into the fluidized-bed reactor 1. In contrast to the drawing, preheating may also be effected in several stages.

Through line 18, granular coal is charged into the gasifier 16, where the grain size of the coal lies in the range from 0.3 to 8 mm. At the same time, O_2 -containing gas (in particu-

lar air or air enriched with O_2) is supplied through line 19, in order to partially oxidize the coal in the gasifier 16. In order to promote the fluidization of solids in the gasifier, fluidizing gas is additionally supplied through line 20. This fluidizing gas comes from the fired heater 23, flows through line 24, and through the branch lines 25, 26, and 27 enters the first and the second reactor 1, 2 as fluidizing gas. The gas in line 24 has temperatures in the range from 600 to 1000°C and preferably 700 to 900°C, its content of $CO + H_2$ lies in the range from 80 to 100 vol-%, and it has a residual CO_2 content of not more than 5 vol-%, preferably not more than 3 vol-%.

Due to the partial oxidation of coal, the gasifier 16 produces char and hot gases, which chiefly contain CO and have temperatures in the range from 900 to 1200°C, when they enter the reactor 1 and carry along the preheated ilmenite from line 15. In the fluidized-bed reactor 1 the temperatures lie in the range from 700 to 1100°C, and usually 900 to 1050°C. From the upper portion of the reactor 1 large amounts of gases and solids are constantly passed through the passage 29 and supplied to a separator 30, e.g. a cyclone. The hot exhaust gases escape via line 6 and, as has already been described, serve to preheat the ilmenite. The separated solids, which include ilmenite and above all char, are delivered via line 31 to the upper portion of the gasifier 16 and from there are recirculated to the reactor 1 through the passage 17. The amount of solids flowing through line 31 per hour is five to twenty^{five} times the amount of solids contained on average in the reactor 1.

From the reactor 1, treated ilmenite and char are continuously withdrawn through line 33, where the ilmenite has a degree of metallization of 50 to 85 %, based on the iron oxides. The mixture of solids is delivered to the second fluidized-bed reactor 2, which in the present case has two cham-

bers 2a and 2b used for reduction and subsequently two chambers 2c and 2d used for cooling. The chambers are separated from each other by weirs 35, across which the solids migrate from one chamber to the next, starting with the first chamber 2a up to the fourth chamber 2d. In each chamber, the solids form a stationary fluidized bed, to which fluidizing gas is supplied through lines 25 and 26 as well as through lines 28 and 28a. The exhaust gas from the second reactor 2 is introduced through line 34 into the first reactor 1. In the first two chambers 2a and 2b the temperatures lie in the range from 600 to 1000°C and preferably 700 to 900°C, the other two chambers 2c and 2d are provided with an indirect cooling 37.

Cooled, reduced ilmenite together with char is withdrawn via line 38, and it can then for instance be supplied to a further treatment and processing to obtain synthetic rutile. For this further treatment it is expedient to sulfidize certain metal components, e.g. manganese, in the reactor 2. For this purpose, the second chamber 2b has a feeding lance 39 for liquid sulfur, which is sprayed into the solids mixture. There is chiefly formed manganese sulfide, which during the further treatment can easily be separated outside the process.

When the crude ilmenite has a relatively high content of FeO, it is necessary to first of all pass it through an oxidation stage, so as to largely convert FeO to Fe₂O₃. This oxidation stage will subsequently be explained with reference to Fig. 2. The ilmenite from the oxidation stage has temperatures of 600 to 1000°C, so that the preheating represented in Fig. 1 by means of the units with the reference numerals 5 to 8 can be omitted. In this case, the hot, oxidized ilmenite is introduced through line 4a indicated in Fig. 1 in broken lines into the gasifier 16, from where it is introduced into the reactor 1. The hot exhaust gas of line 6 will now directly be supplied through line 6a to the waste heat boiler 10.

The process illustrated in Fig. 2 includes an oxidation stage, whose main portion is a circulating fluidized bed comprising the fluidized combustion chamber 50, a connecting passage 51, a cyclone 52 and a return line 53. Fuel, e.g. natural gas, is supplied to the fluidized combustion chamber 50 through line 54, and combustion air, which is also used for fluidization, comes from line 55. As has already been described in conjunction with Fig. 1, the crude ilmenite is delivered through line 4 into the Venturi heat exchanger 5, to which hot gases coming from the cyclone 52 are also supplied through line 56. The gas-solids mixture is delivered through line 7 into the cyclone 8, where the gases flow off through line 8a. The heated ilmenite leaves the cyclone 8 through line 15 and is introduced into the lower portion of the fluidized combustion chamber 50. In the chamber 50, there are provided oxidizing conditions and temperatures in the range from 600 to 1000°C, and through line 56 an exhaust gas is withdrawn, which has an O₂ content of 3 to 10 vol-% and usually 4 to 8 vol-%.

The oxidized and heated ilmenite, which is supplied to the first fluidized-bed reactor 1 via line 4a, has an FeO content of not more than 5 wt-% and preferably not more than 3 wt-%. Through line 27, fluidizing gas rich in hydrogen is supplied to the reactor 1, which fluidizing gas comes from a fired heater 23a, has a temperature in the range from 600 to 1000°C and consists of H₂ for at least 90 vol-%. The reduction of the ilmenite is basically effected in the same way as ex-

explained above in conjunction with Fig. 1. The explanations relating to Fig. 2 can therefore be made short and in part be replaced by using the same reference numerals as in Fig. 1. Hot gases and solids are separated in the cyclone 30, and the solids are recirculated to the reactor 1 through line 31. A small amount of fluidizing gas is constantly supplied to a syphon 31a through line 31b.

The partly reduced ilmenite is introduced through line 33 into the second reactor 2, which now has three chambers 2a, 2b and 2c used for reduction. To the last chamber 2c, liquid sulfur is supplied through the lance 39. Fluidizing gas comes from the fired heater 23b and is distributed through line 26 and introduced into the chambers of the reactor 2. The reduced ilmenite is introduced through line 57 into a separate cooler 58, which has a means 59 for indirect cooling, and to which hydrogen is supplied as fluidizing gas through line 60. This hydrogen freshly supplied to the process can be produced in a plant known per se, which is not represented here.

The hydrogen flowing off the cooler via line 60a is admixed to the exhaust gas of line 61, which has previously been withdrawn from the cyclone 30 through line 62 and cooled in the *heat exchanger* 10. A dry dedusting 11 and a wet dedusting 12 are provided subsequently. Part of the exhaust gas is withdrawn through line 42 and removed from the process, the remaining exhaust gas is passed for a first heating from the blower 48 first through the heat exchanger 10 and then through line 49 into the two fired heaters 23a and 23b, before it is reused in the reactors 1 and 2. Cooled, reduced ilmenite is available in line 38 for further usage.

Example 1

There is employed the procedure illustrated in Fig. 1 (without lines 4a and 6a), where the following amounts of solids are supplied to the plant:

Through line 4:	44.3 t/h ilmenite with 49 wt-% TiO_2 , 48.6 wt-% iron oxides, and 0.1 wt-% moisture;
through line 18:	7566 kg/h coal with 77.3 wt-% C, 4 wt-% ash, 8 wt-% moisture and a lower calorific value of 31000 kJ/kg;

through line 39: 350 kg/h liquid sulfur.

Partly reduced ilmenite with a temperature of 1050°C and a metallization of 85 %, based on the iron oxides, is introduced into the second reactor 2 through line 33; the solids additionally contain a considerable amount of char. The average dwell time of the solids in the first reactor 1 is 15 minutes, because every hour 20 times the amount of solids, based on the average amount of solids in the reactor, is recirculated to the reactor 1 through line 31 and the passage 17. From the second reactor 2 a solids mixture is withdrawn through line 38 in a total amount of 42 t/h, from which 3 t/h char are separated by screening. The reduced ilmenite consists of 56 wt-% TiO_2 , 36.5 wt-% metallic Fe, 1.6 wt-% FeO and the rest gangue (in particular Al_2O_3 and CaO).

The following gases are flowing in the process in accordance with Fig. 1:

Through line 19: 4344 Nm^3/h *technically pure oxygen;*

through line 20: 3000 Nm^3/h fluidizing gas of 750°C;

through line 27: 12000 Nm^3/h fluidizing gas of 750°C;

through lines 25 and 26: 7000 Nm^3/h fluidizing gas of 750°C;

through line 28: 5600 Nm^3/h fluidizing gas of 60°C;
the components of the fluidizing gas are indicated in Table 1, column A.

Through line 9 there are flowing 44000 Nm^3/h exhaust gas with a temperature of 560°C and consisting of the components indicated in Table 1, column B. The exhaust gas in line 14 has been cooled to 35°C, the partial stream withdrawn via line 42

in an amount of $5900 \text{ Nm}^3/\text{h}$ is used in part as fuel for the fired heater 23 and in part for generating steam.

Through line 44, 15 t/h steam are supplied to the regeneration column 43, and $5600 \text{ Nm}^3/\text{h}$ CO_2 are withdrawn through line 45. The gas-solids mixture in the passage 17 has a temperature of 1085°C , $13500 \text{ Nm}^3/\text{h}$ gas and 302 t/h solids including 70 wt-% carbon and 15 wt-% $\text{FeO} \cdot \text{TiO}_2$ flow through the passage. $12660 \text{ Nm}^3/\text{h}$ gas with a temperature of 650°C flow through line 34, the composition is indicated in Table 1, column C.

Table 1

	A	B	C	D	E	F
CO (vol-%)	63	47	55	-	-	-
H_2 (vol-%)	30	22	27	74	70	64
CO_2 (vol-%)	1	16	10	-	-	-
H_2O (vol-%)	3	13	5	0.5	4	10
N_2 (vol-%)	3	2	3	25.5	26	26

Example 2

The procedure is as illustrated in Fig. 2, where 54.2 t/h ilmenite are supplied to the oxidation stage through line 4. The composition of said ilmenite is indicated in Table 2, column A:

Table 2

	A	B	C	D
FeO · TiO ₂ (wt-%)	69.2	3	36.4	7.5
Fe ₂ O ₃ (wt-%)	13.4	47	-	-
TiO ₂ (wt-%)	13.6	47.2	35.7	52.6
Fe (wt-%)	-	-	24.9	36.7
gangue (wt-%)	3.8	2.8	3.0	3.2

The oxidized solids, which are charged into the first reactor 1 through line 4a in an amount of 54.5 t/h and with a temperature of 900°C, have the composition indicated in Table 2, column B. The partly reduced ilmenite, which is charged into the second reactor 2 through line 33 with a temperature of 800°C and in an amount of 48.4 t/h, has a metallization of 65%, based on the iron oxides, and the composition indicated in column C of Table 2. The composition of the cooled product, which is withdrawn with a temperature of 80°C via line 38, is indicated in column D of Table 2. The amount of solids recirculated every hour via line 31 is 15 times the amount of solids contained on average in the first reactor 1.

The gas quantities are as follows:

Through line 54: 1005 Nm³/h natural gas and 1000 Nm³/h exhaust gas from line 42;

through line 55: 37200 Nm³/h air;

through line 8a: 38500 Nm³/h exhaust gas with 10 vol-% O₂;

through line 27: 45500 Nm³/h fluidizing gas with a temperature of 1000°C and the composition indicated in Table 1, column D;

- through line 26: 63700 Nm³/h fluidizing gas with a temperature of 910°C;
- through line 34: 64000 Nm³/h exhaust gas with a temperature of 820°C and the composition indicated in Table 1, column E;
- through line 62: 110600 Nm³/h exhaust gas with a temperature of 800°C and the composition indicated in Table 1, column F;
this exhaust gas leaves the *heat ex-*
*changer*₁₀ with a temperature of 220°C.

~~Claims~~

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process of reducing ilmenite, which has a titanium dioxide content of 45 to 65 wt-% and a content of iron oxides of 30 to 50 wt-%, characterized in that in a first fluidized-bed reactor the ilmenite is partly reduced to a degree of metallization of 50 to 90 %, based on the iron oxides, and in a second reactor, which contains at least one stationary fluidized bed, the ilmenite is reduced to a metallization of 85 to 98 %, based on the iron oxides, where reducing fluidizing gas with temperatures in the range from 600 to 1000°C and a (H₂ + CO) content of 80 to 100 vol-% is supplied to both reactors, that from the upper portion of the first fluidized-bed reactor solids are supplied to a separator together with a gas stream, and in said separator solids are at least partly separated from the gas stream, and separated solids are at least partly recirculated to the first fluidized-bed reactor, where the amount of solids recirculated every hour to the first fluidized-bed reactor is 5 to 25 times the amount of solids contained on average in the first fluidized-bed reactor, and that exhaust gas from the second reactor is introduced into the first reactor.
2. The process as claimed in claim 1, characterized in that the gas stream withdrawn from the separator of the first reactor is cooled, dedusted and partly liberated from steam, and at least part of the gas stream with a CO₂ content of not more than 5 vol-% is recirculated as fluidizing gas.
3. The process as claimed in claim 1 or 2, characterized in that in an oxidation stage the ilmenite is heated to temperatures in the range from 600 to 1000°C by combustion with air in a circulating fluidized bed, before it is charged into the first reactor, and that from the flu-

idized bed of the oxidation stage an exhaust gas with an O₂ content of 3 to 10 vol-% is withdrawn.

4. The process as claimed in claim 3, characterized in that the ilmenite is heated in the oxidation stage, where the FeO content of the heated ilmenite withdrawn from the oxidation stage is not more than 5 wt-%.
5. The process as claimed in claim 1 or any of the preceding claims, characterized in that the second reactor has two to six chambers, where each chamber contains a stationary fluidized bed, and the solids move through all chambers in which iron oxides are reduced.
6. The process as claimed in claim 5, characterized in that the second reactor has at least one chamber, which is designed as cooling chamber with indirect cooling of the solids, and with supply of reducing fluidizing gas.
7. The process as claimed in claim 5 or 6, characterized in that to at least one of the chambers of the second reactor sulfur is supplied for forming metal sulfides.
8. The process as claimed in claim 1 or any of the preceding claims, characterized in that granular coal is partially oxidized in a gasifier by means of O₂-containing gas, and a mixture containing hot gases and char with temperatures of 900 to 1200°C is delivered from the gasifier into the first reactor.

DATED this 23rd day of November 1998.

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Fig. 1

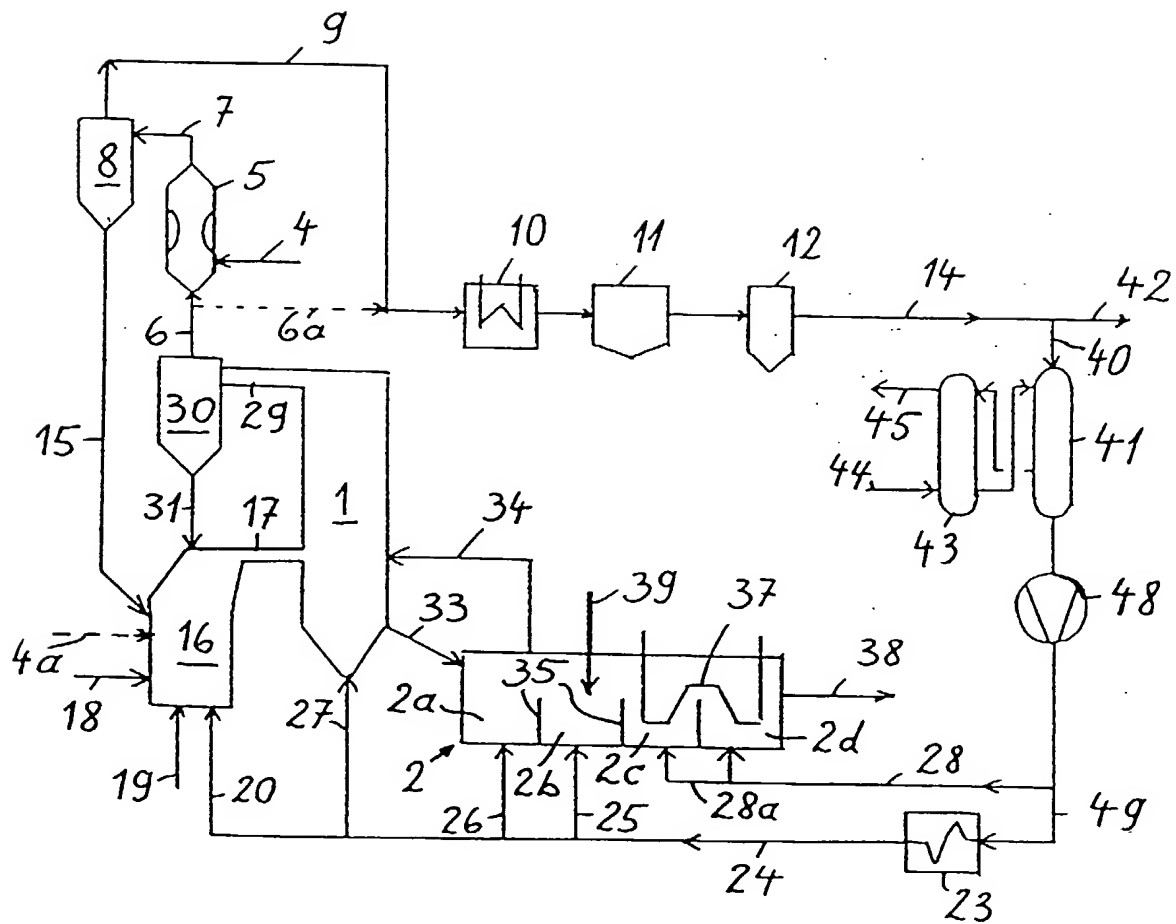


Fig. 2

